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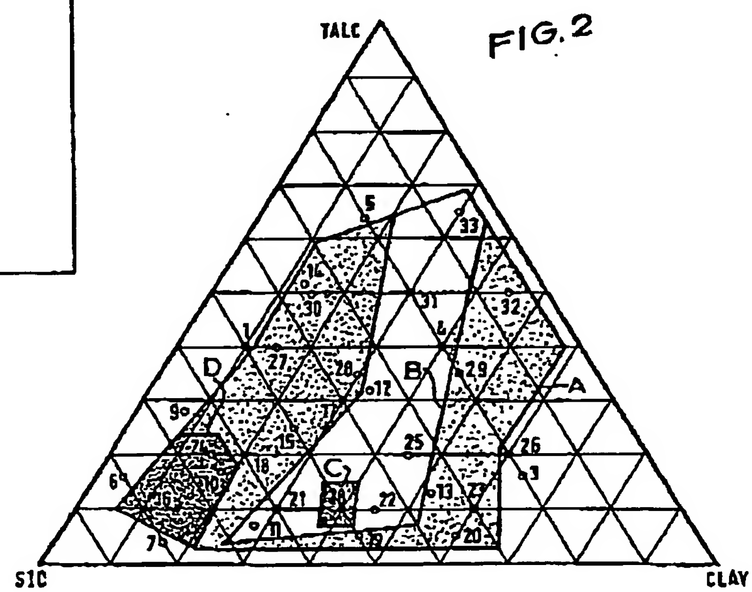
(54) **Silicon carbide ceramic material**

(57) A microwave absorbent ceramic material is disclosed having a modulus of rupture of at least 20 MPa and formed by slip-casting from a slurry containing silicon carbide, clay and talc and firing at a temperature of less than 1200°C, the total quantity of silicon carbide being in excess of 2% w/w and the total quantity of silicon carbide + clay + talc being in excess of 20% w/w of the dry weight of the slurry, preferably the relative amounts in weight percent of silicon carbide (S), clay (C), and talc (T) are defined by those compositions that on a three component S–C–T phase diagram fall within a polygon A having sides defined by lines sequentially joining the points:-

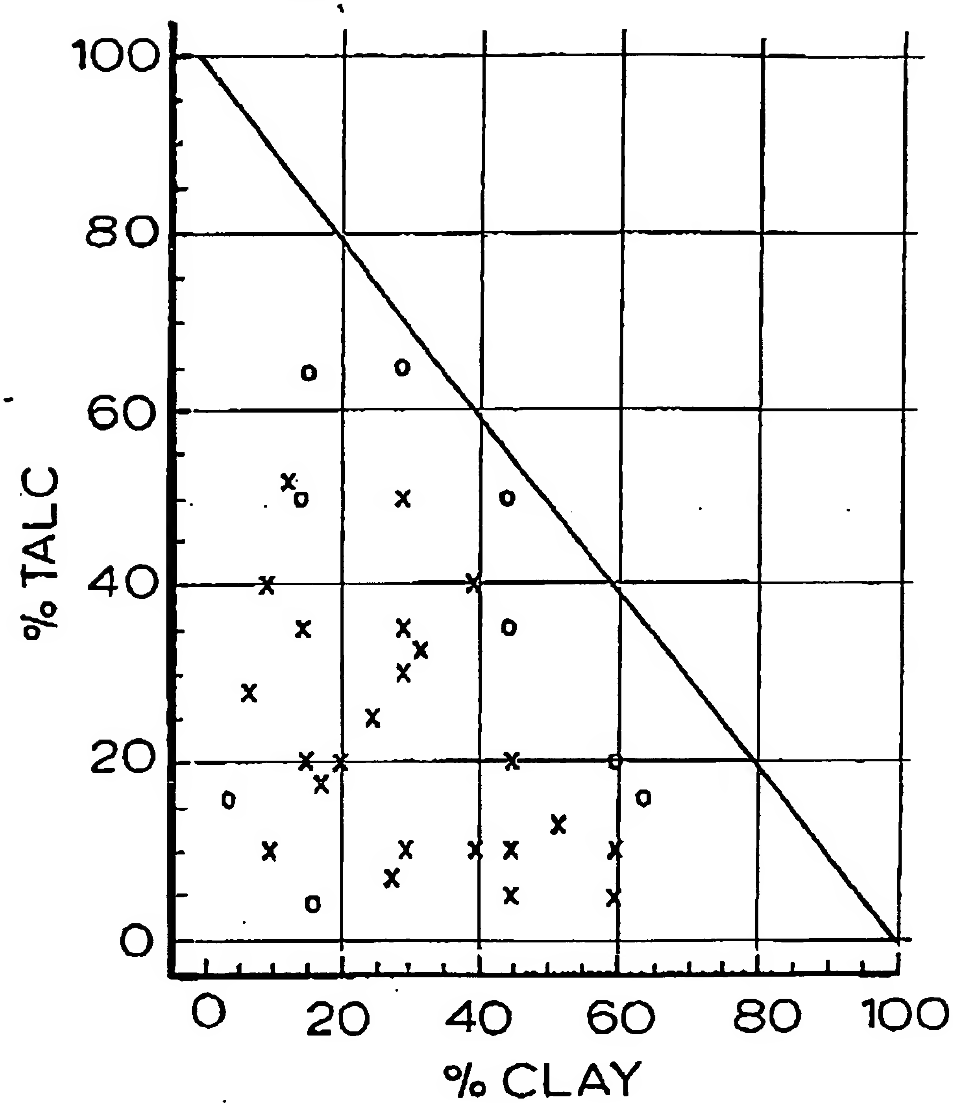
S	T	C
2	40	58
2	69	29
29	60	11
49	40	11
84	10	6
76	3	21
30	3	67
21	21	58
2	40	58

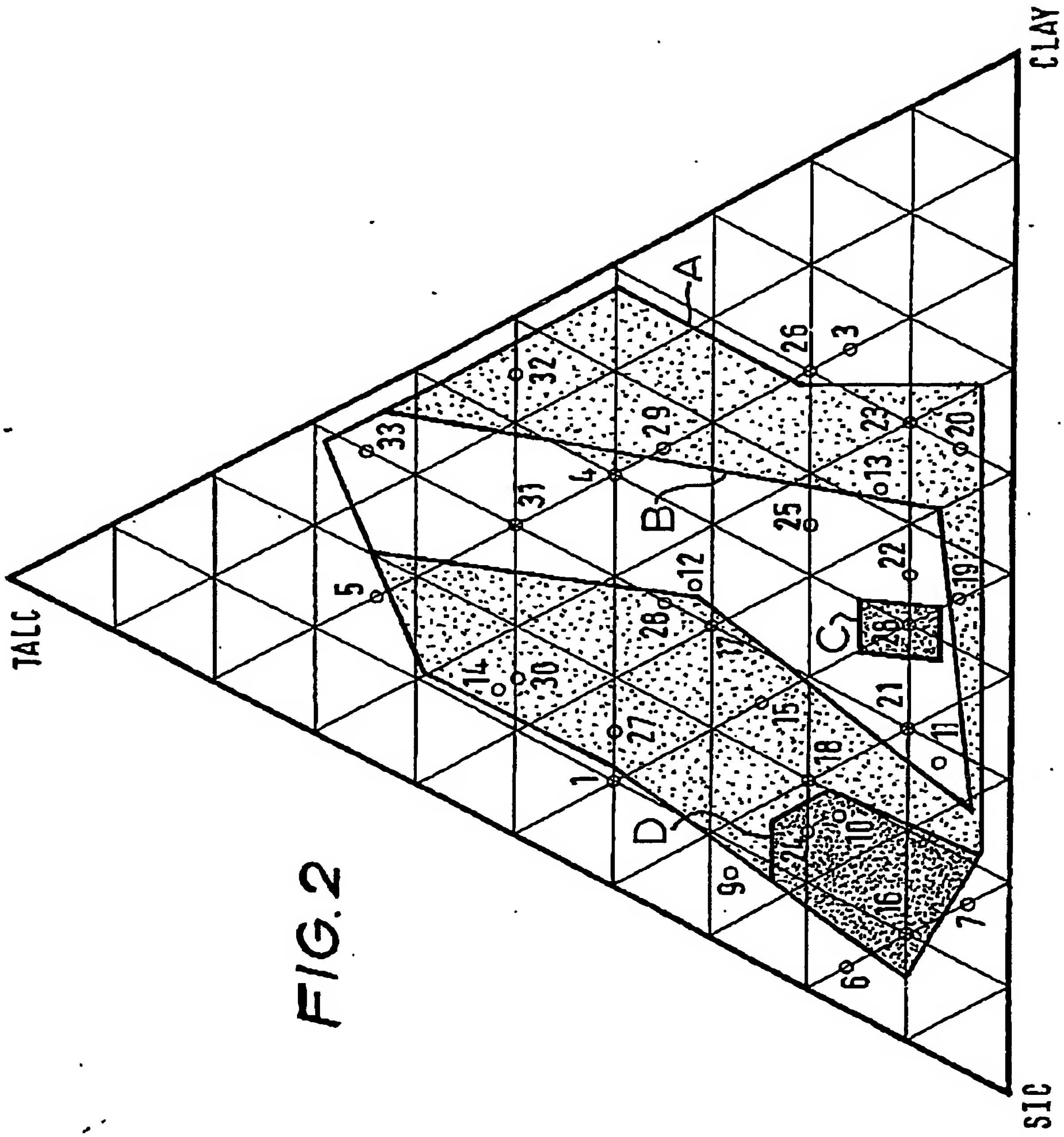
FIG. 2



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

FIG.1




TALC
CLAY
SIC
A
B
C
D
1
2
3
4
5
6
7
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
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27
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29
30
31
32
33

FIG.2

FIG.3

FLEXURAL STRENGTH & CLAY CONTENT

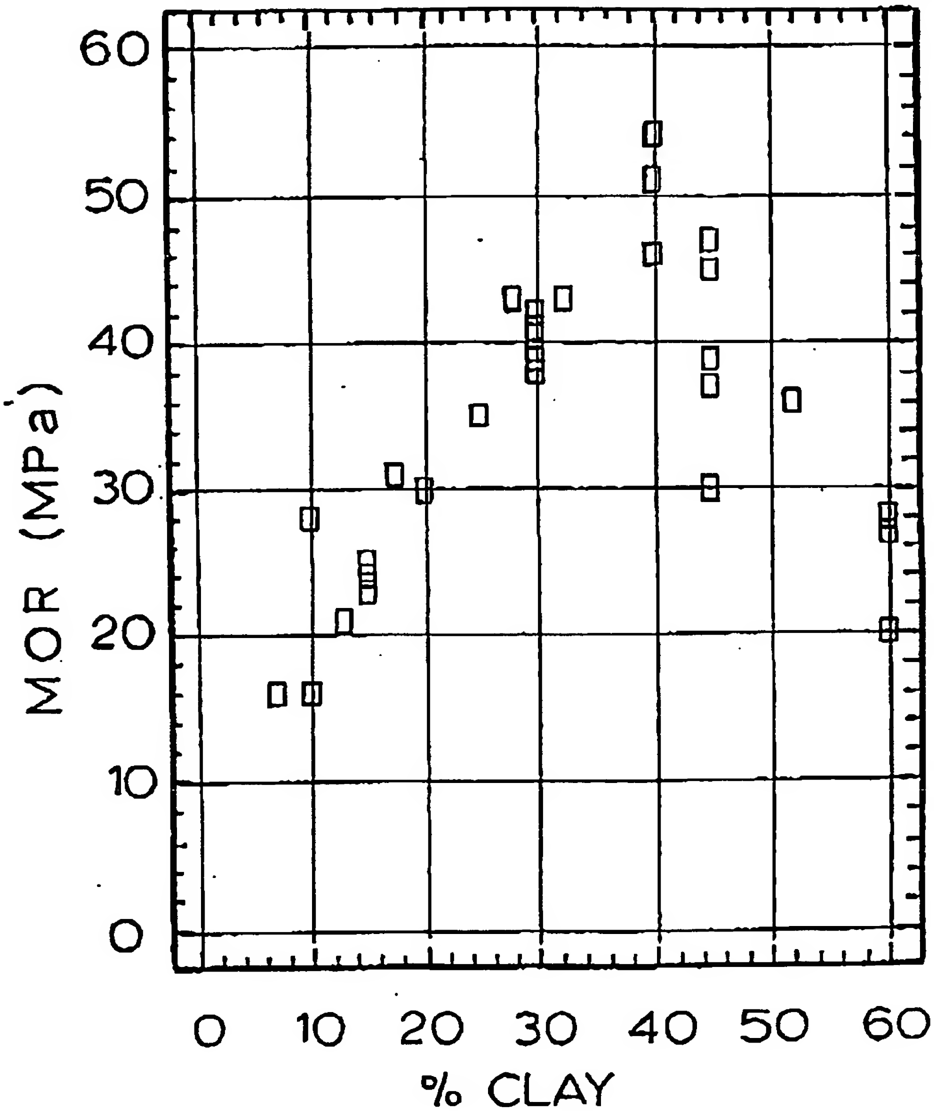


FIG. 4

CASTING RATE & CLAY CONTENT

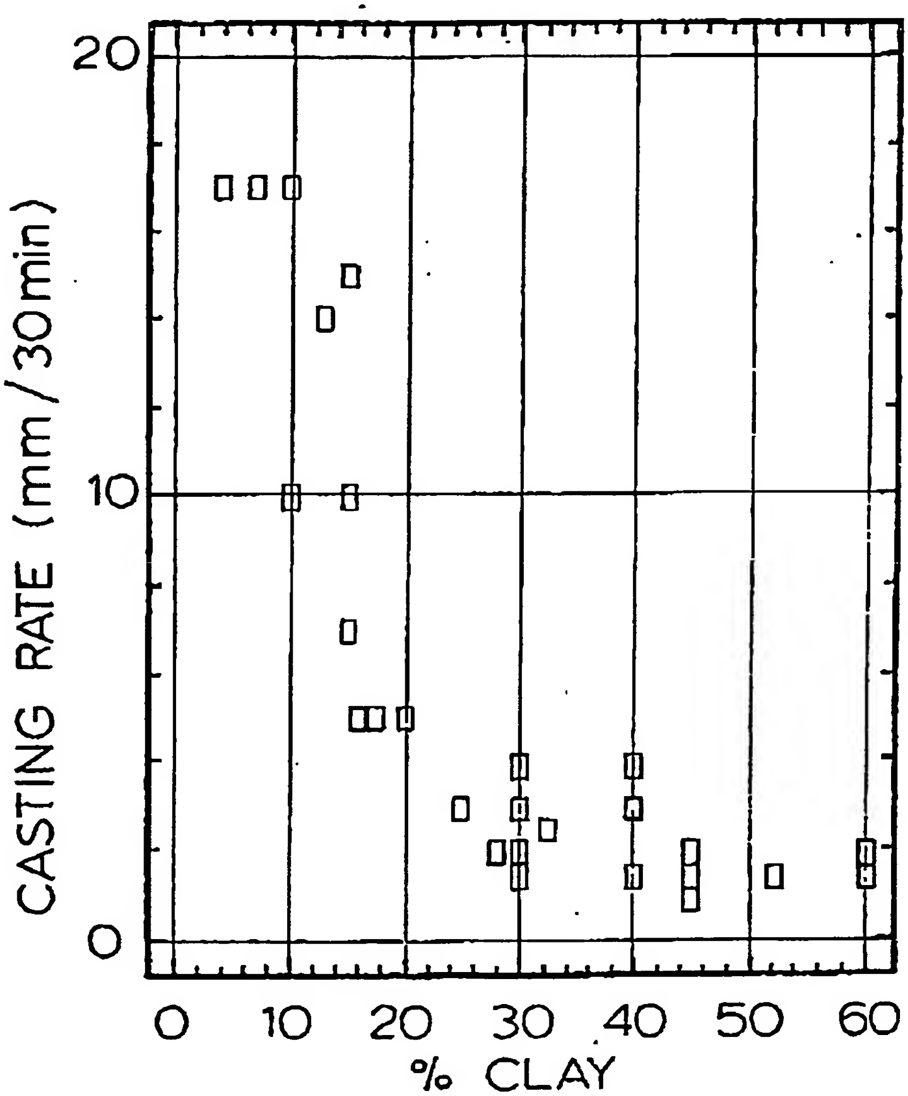
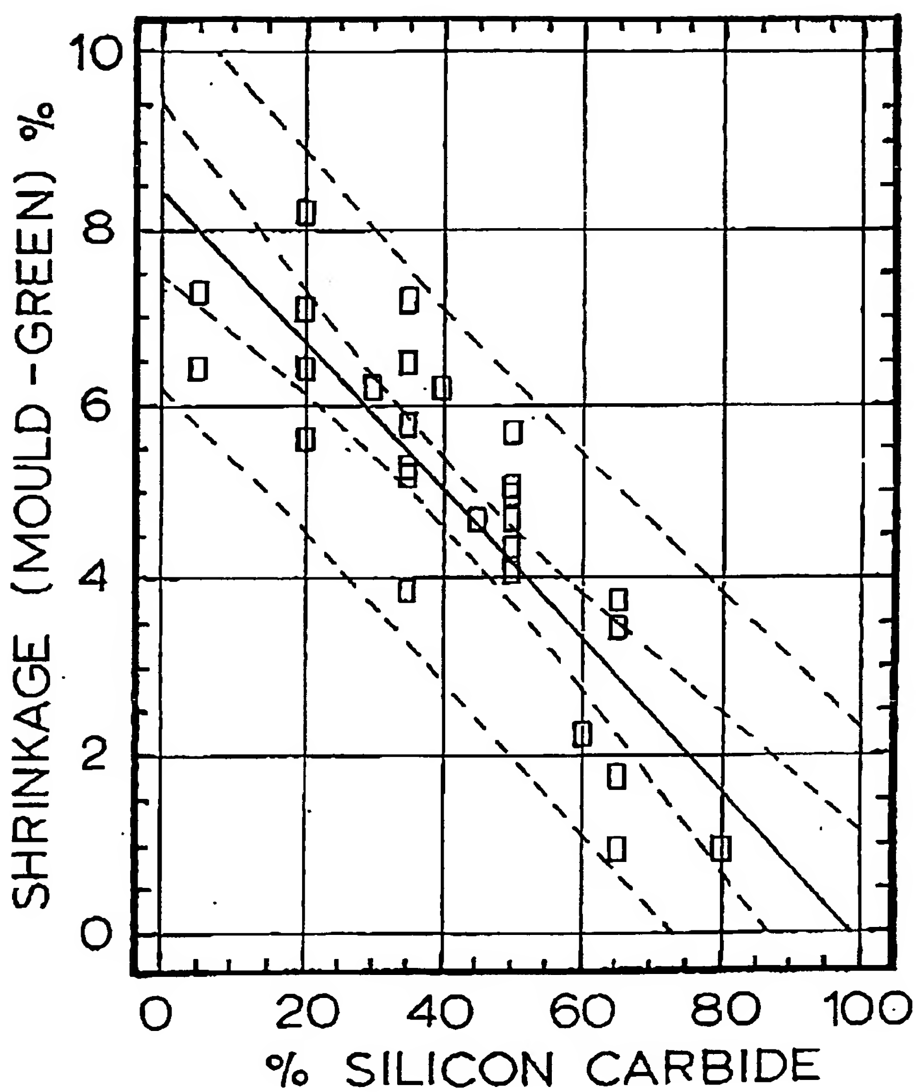


FIG. 5



SHRINKAGE (MOULD - GREEN) %
10
8
6
4
2
0
0
20
40
60
80
100
% SILICON CARBIDE

FIG.6

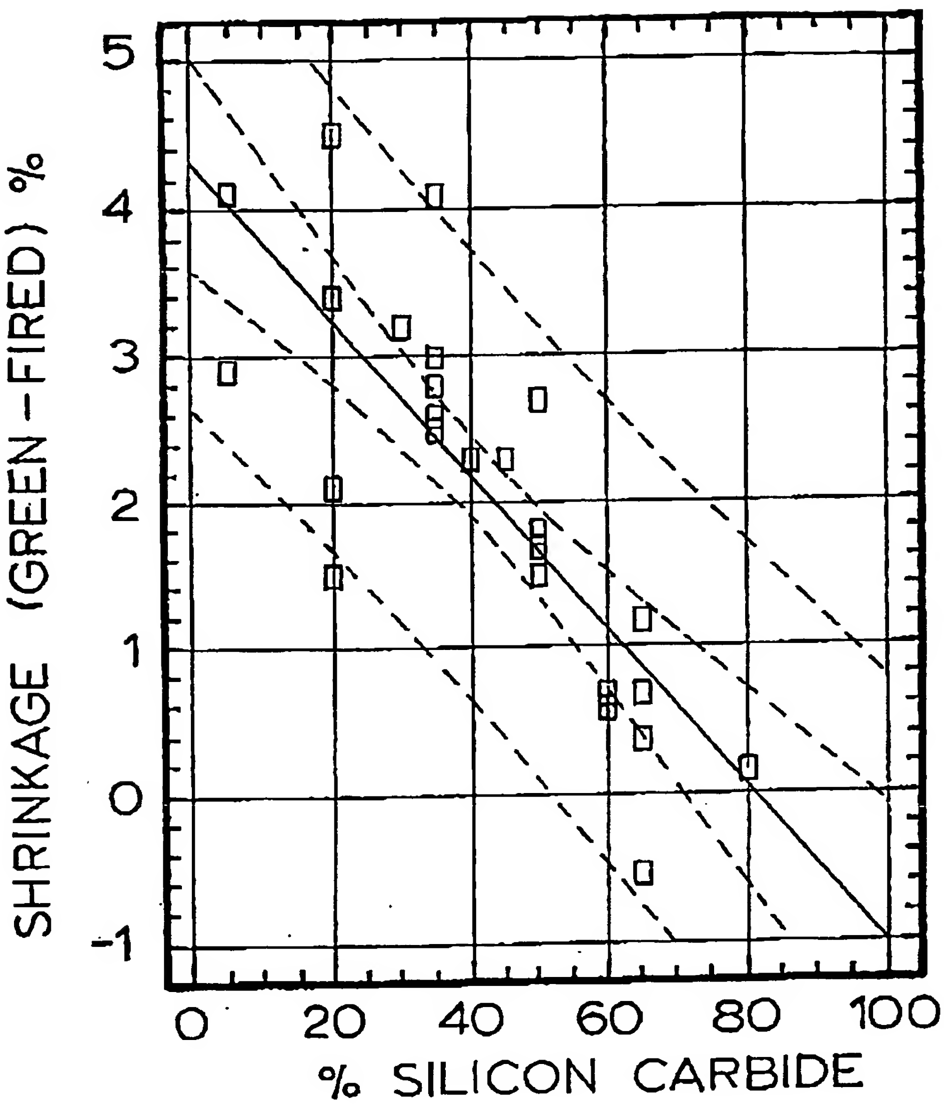

SHRINKAGE (GREEN - FIRED) %
5
4
3
2
1
0
-1
0
20
40
60
80
100
% SILICON CARBIDE

FIG. 7

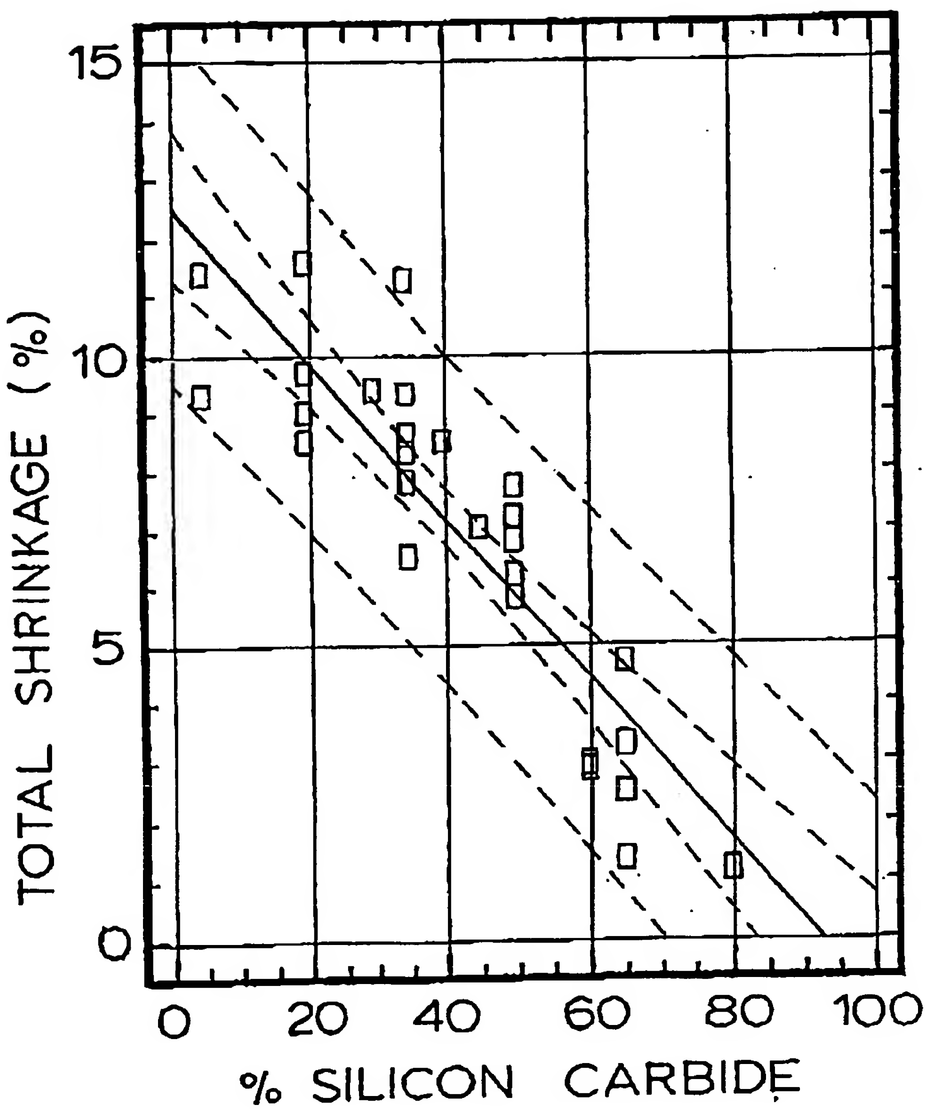
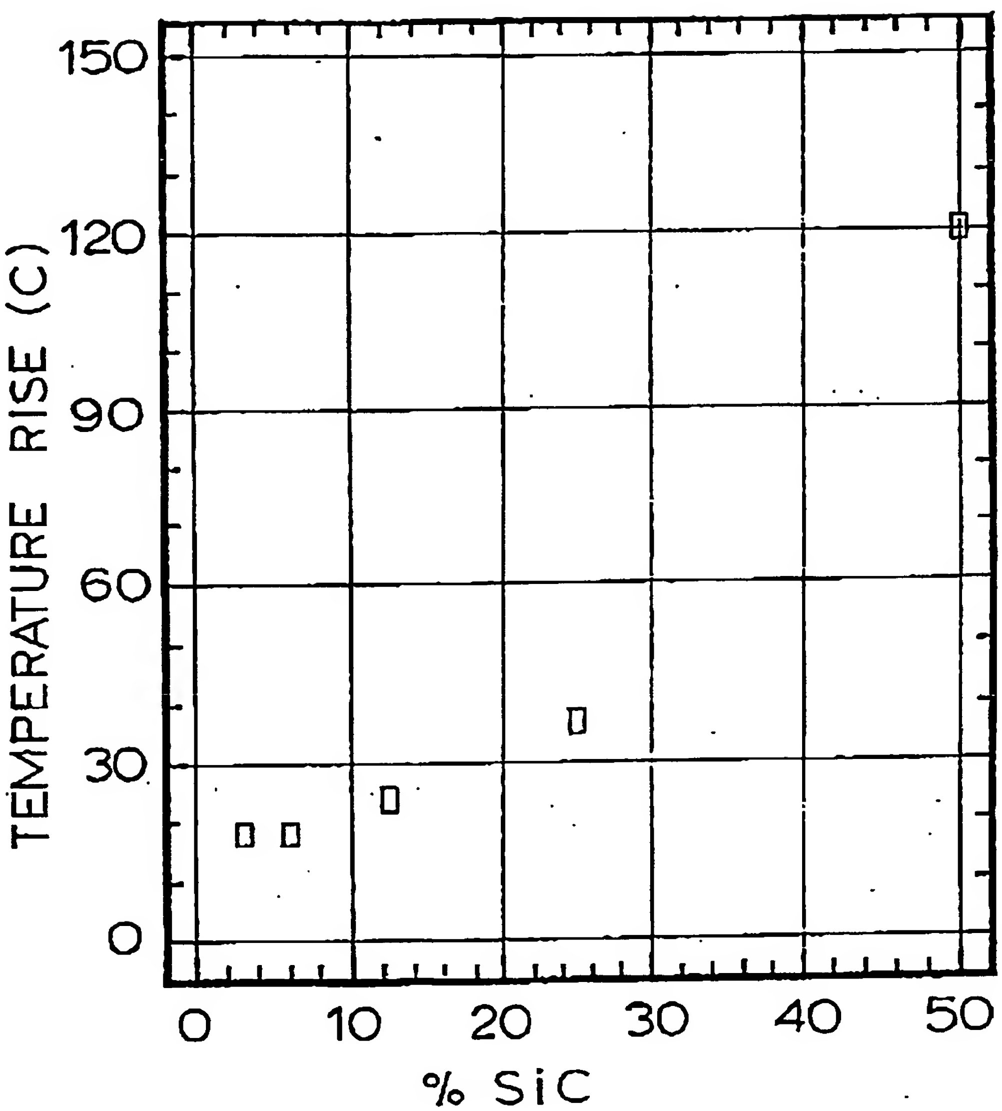


FIG. 8



SLIP-CASTABLE MICROWAVE-HEATABLE SILICON CARBIDE-CONTAINING MATERIALS

This invention relates to slip-castable microwave-heatable silicon carbide-containing materials.

Silicon carbide based materials are made by a variety of methods; sintering of the green compact of silicon carbide under a non-oxidative atmosphere; transformation of a silicon-rich or carbon-rich compact under respectively a carbon-rich or silicon-rich atmosphere; or reaction forming a binder about the silicon carbide.

As an example of this last method U.S. Patent Specification No. 3291759 (J.J. Pitha) discloses a non-linear resistance material formed by:-

making a mixture of approximately 65 weight percent silicon carbide, 14 to 21 weight percent talc, and 21 to 14 weight percent of a porcelain mixture (e.g. clay);

forming said mixture into a shaped article; and

firing the article at a temperature from 1240°C to 1260°C under a hydrogen atmosphere.

The talc and porcelain mixture react to form cordierite which bonds the silicon carbide. The hydrogen atmosphere is necessary to protect the silicon carbide from oxidation.

The same inventor describes similar materials in other U.S. Patent Specification Nos. 3607790 and 3849145.

As a further example of the prior art U.S. Patent 4769346 (K.P. Gadkaree et al) discloses a material comprising silicon carbide whiskers in a barium-stuffed cordierite matrix. The silicon carbide whiskers provide reinforcement of the cordierite material and the material resulting is used for metal extrusion dies and other high temperature products where strength and resistance to creep at temperatures of in excess of 700°C is required. The material described is formed from 5-35% silicon carbide whiskers, the balance being a

cordierite-forming glass. The material is isostatically hot pressed at temperatures in excess of 1300°C and up to 1400°C to form a fired preform, the glass decomposing to form cordierite in the process. The patent gives as a preferred process:-

forming a slurry of the raw materials (silicon carbide whiskers and cordierite-forming glass);

forming a green compact from said slurry by slip-casting or moulding;

isostatically hot-pressing the green compact at temperatures of up to 1400°C to form a fired preform; and

machining the preform to the final desired shape.

The hot pressing described in the patent took place in graphite moulds having molybdenum foil liners and so the atmosphere surrounding the green compact during hot pressing would be non-oxidative. Although the specification states that slip-casting is preferred the example given in the patent does not show slip casting.

The same inventor (K.P. Gadkaree) was also a co-inventor on U.S. Patents 4615987 (K.Chyung et al) and 4776866 (Shih-lu Chen) and in all of these firing took place at a high temperature (1350°C upwards) and in a reducing or non-oxidising atmosphere. If an oxidising atmosphere was used at these temperatures the silicon carbide would oxidise to silica.

United Kingdom Patent Specification No. 1554786 discloses a material comprising silicon carbide and that is fired at temperatures in excess of 1410°C.

Slip casting is a technique, widely used for oxide ceramics, in which a slurry (known as a 'slip') of ceramic material suspended in water or some other liquid carrier, is poured into a mould which is permeable to the liquid carrier. As the liquid carrier is drawn from the slip and permeates the mould a layer of cast material develops on the mould/slip interface. The mould may be heated to accelerate evaporation of carrier from the mould and hence the loss of carrier from the slip to the mould.

The technique of slip-casting allows very fine featured shapes to be formed and thin sectioned shapes such as shells to be made. The process of slip-casting depends critically on the shape of the particles being cast. Whisker or fibre-like particles do not slip cast satisfactorily as a rule since it is difficult for such particles to pack-down in a close packed manner.

European Patent Specification No. 0240160 discloses a dispersant for use in slip-casting material. The ceramics referred to in the specification include silicon carbide but no specific example to use of silicon carbide is given, and indeed the only ceramics for which explicit examples are given are oxide ceramics.

Silicon carbide has been used as a microwave-heatable material in various applications. In particular it has been used as a microwave-heatable former for use in the dip-coating manufacture of e.g. condoms (see International Patent Application No. WO88/09092 [Porous Plastics Limited]).

There is a need for microwave-heatable slip-castable silicon carbide based materials in the manufacture of fine-featured and smooth-finished formers for use in the process of the above mentioned International Patent Application and for other applications.

At the same time there is a need for such materials to be produced at a low cost, with simplicity of processing, and at a low risk to human life (such as is occasioned by firing at elevated temperatures under hydrogen atmospheres).

Accordingly the present invention provides a microwave absorbent ceramic material having a modulus of rupture of at least 20 MPa and formed by slip-casting from a slurry containing silicon carbide, clay and talc and firing at a temperature of less than 1200°C, the total quantity of silicon carbide being in excess of 2 w/o.

Advantageously the relative amounts in weight percent of silicon carbide (S), clay (C), and talc (T) are defined by those compositions that on a three component S-C-T phase diagram fall within a polygon having sides defined by lines sequentially joining the points:-

S	T	C
2	40	58
2	69	29
29	60	11
49	40	11
84	10	6
76	3	21
30	3	67
21	21	58
2	40	58

Further features of the invention will be apparent from the claims in the light of the following description in which reference is made to the drawings in which:-

Fig. 1 shows compositions tested and comprising solely silicon carbide, talc and clay.

Fig. 2 shows the same compositions plotted on a three component phase diagram.

Fig. 3 is a plot of modulus of rupture against clay content.

Fig. 4 is a plot of casting rate against clay content.

Figs. 5,6,7 are plots of mould-green shrinkage, green-fired shrinkage, and total shrinkage respectively against silicon carbide content.

Fig. 8 is a graph of susceptibility to heating in microwaves (shown as a temperature rise) against silicon carbide content.

The applicants made tests on various systems to study the formation of silicon carbide materials and eventually settled on attempting to slip cast silicon carbide. The applicants decided that clay and talc were suitable binder materials since these materials tend to form suspensions easily due to the fineness of particles and also give strength to the 'green' state due to the plate-like nature of the particles.

The binder materials were formed from a mixture of ball clay and talc. Preliminary trials established that a mixture of 70 w/o solids in water could be brought to a castable consistency by the addition of 0.75% Dispex N40 [Trade Mark] deflocculant, a salt of polycarboxylic acid (Allied Colloids Limited, Bradford, England).

Other deflocculants were tried but Dispex N40 was found to be particularly effective. For larger particles an organic binder (3% Dextrine) (National Starch & Chemical Limited, Manchester, England) was also included.

The solid phase consisted of mixtures of clay and talc to which varying amounts of 600 mesh (less than 25μm) silicon carbide was added. Various firing temperatures were tried and satisfactory results were found in the range 1000°C-1200°C. The optimum temperature appeared to be ≈ 1100°C. A firing schedule of 100°C/hour plus 2 hours at temperature was used.

The material has been fabricated by casting into plaster of paris moulds such as are used in the production of ceramic table-ware. Items produced have ranged from small (25mm diameter) crucibles to cylinders 80mm diameter and 200mm high. The thickness of the castings can be controlled from around 1 to 6mm by varying the casting time. Applicants' normal practice was to leave the casts in the moulds at room temperature until they were sufficiently dry and rigid to be removed without distortion. However, it is possible to accelerate this process by drying the moulds and castings at up to 50°C, as is the normal practice in the table-ware industry.

The fired material has a density of around two g/cm^3 (about 80% of theoretical) and an average flexural strength of 30 MPa. The surface finish of the outer surface of the castings, i.e. that which is defined by the mould, is generally good and is a faithful reproduction of the mould.

The detailed results of the tests are shown in Table 1 and Figs. 1 and 2. Fig.1 shows various compositions tested and those indicated by a circle were compositions which either could not be made or which proved unsatisfactory for one reason or another. The applicants have found that a modulus of rupture of the final fired material of 20 MPa is a suitable indicator as to whether or not a material is useful in many applications (particularly in applications such as their use as formers for use in dip coating in accordance with

International Patent Application No. WO88/09092 as mentioned above).

On Figure 2 the polygon referred to generally as A delimits those compositions having a modulus of rupture in excess of 20 MPa and the sides of this polygon are defined by lines sequentially joining the plots:-

S	T	C
2	40	58
2	69	29
29	60	11
49	40	11
84	10	6
76	3	21
30	3	67
21	21	58
2	40	58

The polygon referred to generally as B delimits those compositions having a modulus of rupture in excess of 40 MPa and the sides of this polygon are defined by lines joining the points:-

S	T	C
2	63	35
2	69	29
$15^1/_3$	$64^2/_3$	20
36	32	32
71	4	25
40	7	53
2	63	35

Finally the polygon indicated generally as C encompasses the two compositions found having a modulus of rupture in excess of 50 MPa and the sides of this polygon are defined by lines joining sequentially the points:-

S	T	C
55	7	38
50	7	43
45	15	40
50	15	35
55	7	38

Figure 3 is a graph of flexural strength versus clay content and it can be seen that there does indeed appear to be a peak in strength around the 40% clay mark. The boundaries defined in Figure 2 and in the tables above constitute a selection by the patentees of particular regions having defined modulus of rupture.

For slip casting generally it is preferred that the casting rate be low enough that a reasonable degree of control of the eventual thickness of a cast object can be obtained. Figure 4 shows that for very low clay contents the casting rate tends to be excessively high and this accounts for samples 1, 9 and 6 being excluded from the claimed polygon A as shown in Figure 2.

When it is desired to slip-cast onto a male former (as opposed to normal method of casting into a female mould) then it is desirable that the mould to green shrinkage is less than 2%. In Figure 2 the polygon indicated generally as D is bounded by lines joining sequentially the points:-

S	T	C
84	10	6
76	3	21
62	18	20
62	24	14
$67^2/_3$	24	$8^1/_3$
84	10	6

and the compositions within this polygon have a mould to green shrinkage of less than 2%.

Figure 6 and 7 respectively show the green to fired shrinkage of moulded articles and the total shrinkage of moulded articles as made according to the samples.

All of the above has been discussed in the light of materials comprising only clay, talc and silicon carbide. It is clear that various other constituents could be included without materially affecting the capacity of the material. The applicants believe that the total of silicon carbide plus clay plus talc should exceed 20 w/o of the final material. The applicants have made various materials in which silicon carbide has been progressively replaced with silica.

Figure 8 shows the results of using a material which comprises 25% by weight clay, 25% by weight talc and 50% by weight a mixture of silicon carbide and silica. On the graph the total weight percentage of silicon carbide is plotted against the temperature rise obtained relative to a standard water load when exposed to microwave radiation. It can be seen that even at relatively low concentrations a comparative heating effect is obtained which can be valuable in some applications where a mild excess of heat is required. It will be appreciated that other materials can be inserted other than silica.

Sample	Weight percent SiC	Weight percent talc	Weight percent clay	Casting Rate (mm/30 minutes)	Green Density (g/cm^3)	Fired Density (g/cm^3)	Mould-green Shrinkage (%)	Green-fired Shrinkage (%)	Modulus Rupture (MPa).
1	50	40	10	17	2.0	2.0	5.7	1.5	16
2	50	10	40	3	2.4	2.4	5.0	2.7	51
3	20	16	64						
4	20	40	40	4	2.2	2.2	7.1	4.5	46
5	20	64	16						
6	80	16	4	17					
7	80	4	16	5					
8	50	10	40	2	2.4	2.4	5.1	1.7	54
9	65	28	7	17	2.0	2.0	3.8	-0.5	16
10	65	18	19	5	2.1	2.1	1.8	0.7	31
11	65	7	28	2	2.4	2.5	3.5	1.2	43
12	35	33	33	3	2.3	2.4	5.3	2.5	43
13	35	13	52	2	2.3	2.2	5.2	2.6	36
14	35	52	13	14	2.2	2.1	5.8	2.8	21
15	50	25	25	3	2.2	2.3	4.1	1.7	35
16	80	10	10	10	2.0	2.0	1.0	0.2	28
17	40	30	30	2	2.2	2.2	6.2	2.3	39
18	60	20	20	5	2.1	2.0	2.3	0.6	30
19	50	5	45	2	2.3	2.3	4.4	1.8	39
20	35	5	60	2	2.3	2.4	7.2	4.1	28
21	60	10	30	2	2.3	2.3	2.3	0.7	42
22	45	10	45	1	2.3	2.4	4.7	2.3	47
23	30	10	60	2	2.2	2.2	6.2	3.2	27
24	65	20	15	7	2.1	2.1	1.0	0.4	25
25	35	20	45	2	2.4	2.4	6.5	2.8	45
26	20	20	60	2	2.3	2.0	8.2	1.5	20
27	50	35	15	15	2.1	2.1	4.7	1.5	23
28	35	35	30	3	2.3	2.4	5.3	3.0	33
29	20	35	45	2	2.2	2.1	6.4	2.1	27
30	35	50	15	10	2.0	2.1	3.9	2.6	24
31	20	50	30	4	2.1	2.3	5.6	3.4	41
32	5	50	45	2	2.2	2.2	6.4	2.9	[illegible]
33	5	65	30	4	2.1	2.3	7.3	4.1	41

CLAIMS

1. A microwave absorbent ceramic material having a modulus of rupture of at least 20 MPa and formed by slip-casting from a slurry containing silicon carbide, clay and talc and firing at a temperature of less than 1200°C, the total quantity of silicon carbide being in excess of 2% w/w and the total quantity of silicon carbide + clay + talc being in excess of 20% w/w of the dry weight of the slurry.

2. A microwave absorbent ceramic material as claimed in claim 1 in which the relative amounts in weight percent of silicon carbide (S), clay (C), and talc (T) are defined by those compositions that on a three component S-C-T phase diagram fall within a polygon having sides defined by lines sequentially joining the points:-

S	T	C
2	40	58
2	69	29
29	60	11
49	40	11
84	10	6
76	3	21
30	3	67
21	21	58
2	40	58

3. A microwave absorbent material as claimed in claim 2 in which the points are:-

S	T	C
2	63	35
2	69	29
$15^1/_3$	$64^2/_3$	20
36	32	32
71	4	25
40	7	53
2	63	35

4. A microwave absorbent material as claimed in claim 3 in which the points are:-

S	T	C
55	7	38
50	7	43
45	15	40
50	15	35
55	7	38

5. A microwave absorbent material as claimed in claim 2 for slip casting onto a male former and in which the points are:-

S	T	C
84	10	6
76	3	21
62	18	20
62	24	14
$67^2/_3$	24	$8^1/_3$
84	10	6

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